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The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating

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HIGHLIGHTS

- ▶ Microwave pyrolysis of torrefied biomass favored phenols and sugars production.
- ▶ Organic acids were greatly reduced in bio-oils from pyrolysis of torrefied biomass.
- ▶ Bio-oil from pyrolysis of torrefied biomass contained up to 7.5 area% hydrocarbons.
- ▶ Syngas from pyrolysis of torrefied biomass was rich in H_2, CH_4, and CO.

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ABSTRACT

Microwave pyrolysis of torrefied Douglas fir sawdust pellet was investigated to determine the effects of torrefaction on the biofuel production. Compared to the pyrolysis of raw biomass, the increased concentrations of phenols and sugars and reduced concentrations of guaiacols and furans were obtained from pyrolysis of torrefied biomass, indicating that torrefaction as a pretreatment favored the phenols and sugars production. Additionally, about 3.21–7.50 area% hydrocarbons and the reduced concentration of organic acids were obtained from pyrolysis of torrefied biomass. Torrefaction also altered the compositions of syngas by reducing CO_2 and increasing H_2 and CH_4. The syngas was rich in H_2, CH_4, and CO implying that the syngas quality was significantly improved by torrefaction process.

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1. Introduction

Fossil oils are the primary energy resource in the past and today's transportation fuel supply. However, the fossil oils are not renewable and the application of fossil oils brings environmental problems, for example, that carbon dioxide emission in the combustion of fossil oils contributes to the global warming. These problems motivate scientists and researchers to look for the renewable energy resources. Biomass is one of important and large amount renewable fuel sources. Unlike the fossil oils, biomass is planted and collected annually that can provide a continuous energy supply. Biomass is considered carbon neutral as its carbon is recycled from the atmosphere (Ragauskas et al., 2006). Biomass are playing important role in energy supplies. In US, the potential capacity of biomass is up to 1.3 billion dry tons annually which can replace a large portion of current petroleum consumption (Perlack et al., 2005).

Pyrolysis is a thermal chemical technology conducted at temperatures ranged from 400 to 600 °C in the absence of oxygen (Scott and Piskorz, 1984). During pyrolysis biomass is heated and decomposed to produce bio-oil, biochar, and syngas. In recently years, biomass pyrolysis has received interests to produce high yield liquids as they are promising hydrocarbon biofuels which can be easily transported, burnt directly in thermal power stations, or upgraded to obtain a hydrocarbon fuel. Traditional biomass pyrolysis processes such as fixed and fluidized bed reactors, use heating provided by heated surface, sands, and hot gas (Meier and Faix, 1999; Czernik and Bridgwater, 2004; Mohan et al., 2006). The particle size of biomass feed material is an important parameter in determining the efficacy of pyrolysis. Very fine feedstock is required by conventional pyrolysis in order to obtain high heating rates (Sensoz et al., 2000; Yi et al., 2008; Moghtaderi et al., 2004). Pyrolysis oil and char yields were found to be largely dependent on particle sizes (Sensoz et al., 2000). Microwave pyrolysis is one of the thermo-chemical technologies by heating biomass with microwave irradiation. The major advantage of the microwave heating process over conventional heating methods is the nature of internal fast and uniform heating by microwave irradiation

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(McKendry, 2002; Miura et al., 2000). Previous reports showed that biomass microwave pyrolysis can be induced in large-size particles and produce high bio-oil yields which are similar to the fluidized bed pyrolysis (Lei et al., 2009; Ren et al., 2012). Microwave pyrolysis has been successfully applied to processing plant residues (Lei et al., 2009; Yu et al., 2007; Huang et al., 2010), wood (Miura et al., 2000, 2004; Ren et al., 2012), and sewage sludge to produce bio-oil, gas, and biochar (Dominguez et al., 2006; Tian et al., 2010).

Bio-oils are carbon based liquid which has some similar properties to the petroleum fuel such as low solid content and low viscosity (Czernik and Bridgwater, 2004; Mohan et al., 2006). Bio-oils have high carbon content and can be combusted directly in boilers, gas turbines, and slow and medium-speed diesel engines for heat and power applications. Bio-oils also have low nitrogen and sulfuric content. Therefore, bio-oils are considered to be very promising hydrocarbon fuels. However, the crude bio-oils contain high moisture content which is up to 15−30 wt.%. The elemental analysis showed that the bio-oils contain about 35−40 wt.% of oxygen which is much higher than that of petroleum fuels. The pH value of crude bio-oils is around 2.5 due to the existence of organic acids. The heating value of bio-oil is ~17 MJ/kg which is lower than half of energy from petroleum fuels. These properties make the bio-oil immiscible with gasoline and difficult to integrate into the current petroleum refinery system.

Torrefaction is a mild thermal chemical technology at relatively low reaction temperature of 200–300 °C to improve the biomass quality (Bergman and Kiel, 2005). The mechanisms analysis for biomass torrefaction indicates that the hemicelluloses are deeply decomposed and cellulose and lignin are partially decomposed. Below the temperature of 250 °C the limited decomposition and carbonization of hemicelluloses were mainly involved accompanied with the minor lignin and cellulose decomposition. But at the temperatures over 270 °C, further carbonization of hemicelluloses and limited decomposition and carbonization of lignin and cellulose occurred. The strong torrefaction with a serious weight loss occurred in the temperature regime above 275 °C (Bridgeman et al., 2008; Chen and Kuo, 2011; Prins et al., 2006a). Thus, during torrefaction the moisture of biomass will be removed by evaporation and some organic acids such as acetic acid will be driven off from biomass by the hemicelluloses decomposition. The O/C ratio of torrefied biomass will be significantly decreased as the decomposition of hemicelluloses and dehydration of cellulose and lignin occurred during torrefaction (Prins et al., 2006b). Therefore, torrefied biomass contains less moisture and high carbon content. These characteristics benefit the further process such as combustion and gasification. It has been proved that torrefied biomass can generate electricity with a similar efficiency to coal and improve the syngas quality by gasification (Lipinsky et al., 2002; Bergman et al., 2005a,b).

The objective of this study was to investigate microwave pyrolysis of torrefied Douglas fir sawdust pellets. The effects of torrefaction conditions on yields of bio-oil, syngas, and biochar were determined. The characteristics of bio-oil and syngas from torrefied biomass microwave pyrolysis were determined by GC/MS and GC respectively.

2. Methods

2.1. Materials

Douglas fir sawdust pellets purchased from Bear Mountain Forest Products Inc. (USA) were used as raw materials for torrefaction. The pellets were made from 100% natural Douglas fir wood sawdust. The raw pellets had an average diameter of 6 mm and an average length of 10 mm. Proximate and elemental analysis of raw Douglas fir pellet were showed in Table 1. The higher heating value (HHV) of raw Douglas fir pellet was 19.4 MJ/kg.

Table 1
Proximate and elemental analyses of Douglas fir pellet.

Characteristics	Douglas fir pellet
Proximate analysis (wt.%)	
Moisture	4.82
Volatile matter	76.08
Fixed carbon	18.89
Ash	0.21
Elemental analysis (wt.%)	
Carbon	47.9
Hydrogen	6.55
Nitrogen	0.08
Oxygen	45.57
HHV (MJ/kg)	19.4

2.2. Torrefied biomass preparation

The torrefaction of Douglas fir pellets was conducted in a batch microwave oven which was described in our previous report (Lei et al., 2009; Ren et al., 2012). Two-hundred grams of Douglas fir pellets was placed in a half liter quartz flask inside of the microwave oven. The power input for the microwave oven was 600 W at 2450 MHz. The reaction temperature was measured by an infrared temperature sensor attached to the microwave reactor manufactured by Sineo Microwave Chemistry Technology Company (Shanghai, China). After reaching desired reaction temperatures, the microwave reactor equipped with automatic temperature/power control used a minimum power (e.g. 0–100 W) to maintain the desired reaction temperatures. Two variable conditions, reaction temperature and time were used in the torrefaction process. A central composite experimental design (CCD) was employed for evaluating the effects of torrefaction conditions on the biofuel production of torrefied biomass pyrolysis. The reaction temperatures were ranged from 240 to 310 °C with the central point of 275 °C and the step changes of 25 °C. The reaction time was ranged from 8 to 22 min with the central point of 15 min and the step changes of 5 min based on CCD. Total 11 experiments with four axial points ($\alpha = 1.41$) and three replications at the center points were employed for the torrefied biomass preparation (Table 2).

2.3. Torrefied biomass pyrolysis

Torrefied biomass pyrolysis was performed in the batch microwave oven which was the same apparatus used for the biomass torrefaction process. The power input for microwave pyrolysis was used at the 700 W. About 100 g of torrefied biomass was placed in a half liter quartz flask inside of the microwave oven. Microwave pyrolysis of torrefied biomass was conducted at the reaction temperature of 480 °C and reaction time of 15 min as in this reaction condition the highest bio-oil yield of biomass microwave pyrolysis can be obtained according to the previous experiment (Ren et al., 2012). During pyrolysis the heavier volatiles were condensed into liquids as bio-oils and the lighter volatiles escaped as syngases at the end of the condensers where they were either burned or collected for analysis. Char was left in the quartz flask. The weight of syngas product was calculated by difference using following equation:

$$\begin{aligned}\text{Weight of syngas} &= \text{initial torrefied wood pellet mass} \\ &\quad - \text{bio-oil mass} - \text{biochar mass} \qquad (1)\end{aligned}$$

Table 2
Summary of torrefaction conditions and results.

Run #	Torrefaction conditions		Weight loss in torrefaction (wt.%)	HHVs of torrefied biomass (MJ/kg)	Products yield from pyrolysis (wt.% based on torrefied biomass)			Products yield from torrefaction and pyrolysis (wt.% based on raw biomass)		
	Temperature (°C)	Time (min)			Bio-oil	Syngas	Biochar	Bio-oil	Syngas	Biochar
1	250	10	16.85	20.9	37.35	32.42	30.23	44.17	30.69	25.14
2	300	10	40.90	23.25	22.56	34.37	43.07	45.91	28.64	25.45
3	250	20	23.48	21.61	32.23	34.02	33.76	42.32	31.85	25.83
4	300	20	47.39	25.07	17.14	33.25	49.61	45.37	28.53	26.10
5	240	15	17.62	21.28	39.42	29.45	31.13	46.54	27.82	25.65
6	310	15	43.93	23.36	21.17	32.03	46.80	44.48	29.27	26.24
7	275	8	27.69	21.59	40.25	24.13	35.63	51.18	23.05	25.76
8	275	22	34.07	23.55	28.28	31.26	40.47	45.43	27.89	26.68
9	275	15	29.16	22.41	30.97	32.33	36.70	45.35	28.65	26.00
10	275	15	31.81	23.01	31.49	30.08	38.43	47.03	26.76	26.21
11	275	15	31.71	22.82	32.13	28.62	39.25	46.50	26.69	26.80
12	Raw biomass			19.6	53.42	19.48	27.1			

2.4. GC/MS analysis for bio-oil

Chemical compositions of the bio-oil were determined using an Agilent 7890A GC/MS with a DB-5 capillary column. The GC was programmed at 45 °C for 3 min and then increased at 10 °C/min to 300 °C and finally held isothermal for 10 min. The injector temperature was 300 °C and the injection size was 1 L. The flow rate of the carrier gas (helium) was 0.6 mL/min. The ion source temperature was 230 °C for the mass selective detector. The compounds were identified by comparing the spectral data with the NIST Mass Spectral library.

2.5. GC analysis for syngas

The chemical compositions of syngas were determined by a Carle 400 gas chromatography (GC) system with a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Characterization of torrefied biomass

Torrefaction conditions such as reaction temperature and time significantly affected the degree of biomass component decomposition (Bergman et al., 2005a). In this research, the mass loss of raw biomass at different torrefaction conditions was determined and the results were similar to the previous reports (Bridgeman et al., 2008; Chen and Kuo, 2011; Prins et al., 2006a). The mass loss of Douglas fir pellet was significantly increased with the increase of reaction temperature and time (Table 2). The mass weight loss was observed from 16.85 to 34.07 wt.% at the temperature range of 240 to 275 °C. And a very large weight loss, up to 40.9–47.39 wt.% was observed at the temperatures over 300 °C which indicated that cellulose and lignin were severely damaged.

Torrefaction process can remarkably improve the heating value of biomass. The HHVs of torrefied biomass were ranged from 20.3 to 25.4 MJ/kg and increased with the increase of reaction temperature and time (Table 2). The highest HHV of torrefied biomass was 31% more than that of raw biomass, which was observed at reaction temperature of 300 °C and reaction time of 20 min. The heating values of torrefied biomass were significantly greater than those of raw biomass and similar to those of coals. According to the weight loss and heating values of torrefied biomass, the energy yields of torrefied biomass were calculated. The energy yields of torrefied biomass were ranged from 67.69% to 90.6% which indicated that most energy of raw biomass was maintained in the torrefied biomass that will benefit the further process.

3.2. Mass balance in torrefied biomass pyrolysis

Total 11 samples from torrefaction pretreatment plus one raw biomass were pyrolyzed. The products yield distributions were showed in Table 2. The products yield of torrefied biomass pyrolysis had high relationship with the torrefaction process. The bio-oil yields from pyrolysis of torrefied biomass were ranged from 21.17 to 40.25 wt.% based on torrefied biomass which was much less than that from pyrolysis of raw biomass; while the syngas and biochar yields were ranged from 24.13 to 34.37 wt.% and 31.13 to 49.61 wt.% based on torrefied biomass, respectively, which were much higher than those from pyrolysis of raw biomass. However, the total bio-oil yields from both torrefaction and pyrolysis based on raw biomass were ranged from 42.32 to 51.18 wt.% (Table 2) while the bio-oil yields from pyrolysis of raw biomass were from 31.5% to 53.5% based raw biomass depending on pyrolysis conditions (Ren et al., 2012), indicating that the total bio-oils yield from combined torrefaction and pyrolysis processes was comparable with the bio-oil yield from pyrolysis of raw biomass. The total syngas yields based on raw biomass were increased compared to that from pyrolysis of raw biomass, suggesting that the combined processes tend to produce more syngas.

Further analysis showed that the torrefaction temperature and time had significantly effects on the products yield of torrefied biomass pyrolysis. The bio-oil yields based on torrefied biomass were significantly decreased with the increase of the torrefaction temperature and time (Fig. 1). It might be attributed to the removing of components such as hemicelluloses and partial cellulose and lignin during the torrefaction. The syngas yields based on torrefied biomass from pyrolysis of torrefied biomass were slightly increased with the increase of torrefaction temperature while the biochar yields (based on torrefied biomass) were greatly increased with the increase of torrefaction temperature. The torrefaction time had minor effects on syngas and biochar yields (Table 2). However, the biochar yields based on raw biomass from combined processes were slightly lower than that from biomass direct pyrolysis and relatively stable at different torrefaction conditions (Table 2).

3.3. GC/MS analysis for bio-oil

To further understand the chemical reactions of microwave pyrolysis of torrefied biomass and obtain more insight of the effects of torrefaction on bio-oils, the compositions of bio-oils were characterized by GC/MS and categorized into 10 groups based on bio-oil's functional groups (Fig. 2). The compositions of the bio-oil from pyrolysis of torrefied biomass were obviously different from that obtained from pyrolysis of raw biomass. The guaiacols from pyrolysis of raw biomass were the largest amount chemicals

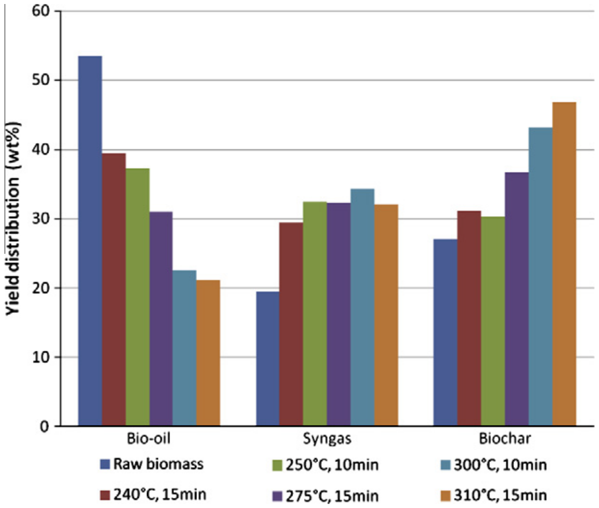

Fig. 1. The effects of torrefaction temperatures on the products yield (based on torrefied biomass) of torrefied biomass pyrolysis.

which contributed to 50.90 area% of the total. Comparing to that from pyrolysis of raw biomass, the guaiacols in the bio-oil from pyrolysis of torrefied biomass ranged from 27.82% to 38.26% were significantly decreased. The phenols from pyrolysis of torrefied biomass were ranged from 16.16 to 29.95 area% which was significantly increased compared to that from pyrolysis of raw biomass which was observed at 8.73 area%. The other two large amount chemicals observed in the bio-oil from pyrolysis of torrefied biomass were furans and sugars. The amounts of furans from pyrolysis of torrefied biomass were ranged from 7.96 to 14.15 area% which was obviously lower than that from pyrolysis of raw biomass. On the contrary, the amounts of sugars from pyrolysis of torrefied biomass ranged from 5.9 to 20.71 area% were significantly higher than that from pyrolysis of raw biomass which was 2.83 area%. These results indicate that the torrefaction process favored the phenols and sugars production by torrefied biomass pyrolysis. The acids from torrefied biomass pyrolysis ranged from 1.6 to 2.78 area% were also decreased compared to that from pyrolysis of raw biomass. The same findings were reported in previous research that investigated the characteristics of bio-oil from torrefied biomass using fluidized bed pyrolysis (Meng et al., 2012). Hydrocarbons are important chemicals for transportation fuels. No hydrocarbons were detected in the bio-oil from pyrolysis of raw biomass. But in this research, about 3.21–7.5 area% hydrocarbons were observed which was not reported in previous work (Meng et al., 2012). These hydrocarbons might have benefits for further bio-oil refinery process such as reducing consumption of hydrogen.

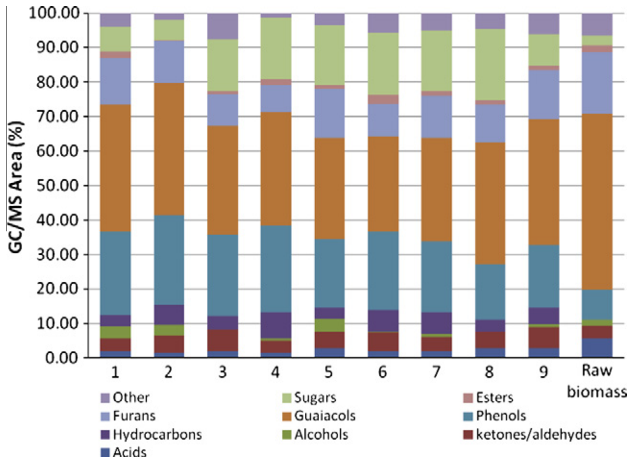

Fig. 2. Chemical composition distribution of bio-oils from microwave pyrolysis of torrefied biomass.

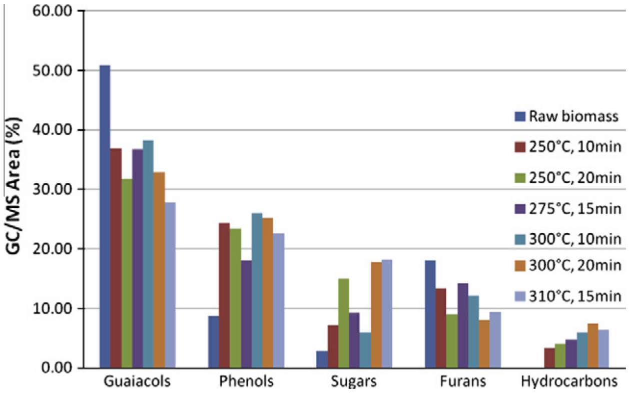

Fig. 3. The effects of torrefaction on the chemical composition of bio-oils from torrefied biomass pyrolysis.

The changes of chemical compositions of bio-oils at the different torrefaction temperature and time were showed in Fig. 3. The guaiacols from torrefied biomass were not significantly changed with the torrefaction temperature below 300 °C; but guaiacols were greatly decreased at the torrefaction temperature of 310 °C. However, the guaiacols were significantly decreased with the increase of reaction time at the same torrefaction temperature. The amounts of phenols from torrefied biomass pyrolysis were relatively stable as only slight changes were observed at different torrefaction processes. The total phenolic compounds showed a decreasing trend especially at the high torrefaction temperature and long reaction time. This result was consistent with the very large weight loss observed at the temperature over 300 °C in which lignin might be partially decomposed. The sugars were increased with the increase of torrefaction temperature and time while the furans were decreased. The hydrocarbons were also increased with the increase of torrefaction temperature and time. The maximum sugars and hydrocarbons were 20.71 and 7.5 area% observed at the torrefaction temperature of 275 °C and time of 22 min and 300 °C and 20 min, respectively.

3.4. GC analysis for syngas

Syngas was one of important co-products from microwave pyrolysis of biomass as the high contents of valuable gases were detected in previous reports (Lei et al., 2009; Ren et al., 2012). Thus, characterizing the compositions of the syngas will help better understand the reaction mechanism of torrefied biomass microwave pyrolysis and explore its potential utilization.

The syngas from pyrolysis of raw biomass was mainly composed of carbon dioxide, carbon monoxide, methane, and short-chain hydrocarbons. Carbon monoxide was the largest amount of the chemicals in the syngas which contributed to about 44% (v/v). The content of carbon dioxide was about 26% (v/v). The contents of methane and short chain hydrocarbons were relatively low which contributed to about 6% (v/v) and 5% (v/v) of the syngas, respectively. There was no hydrogen detected in the gas products of raw Douglas fir pellet microwave pyrolysis. Comparing to syngas from pyrolysis of raw biomass, the compositions of syngas from pyrolysis of torrefied biomass were significantly different. Carbon monoxide was still the largest amount of chemical in the syngas from pyrolysis of torrefied biomass which was ranged from 25.98% to 45.30% (v/v) varied with the torrefaction condition significantly. The contents of

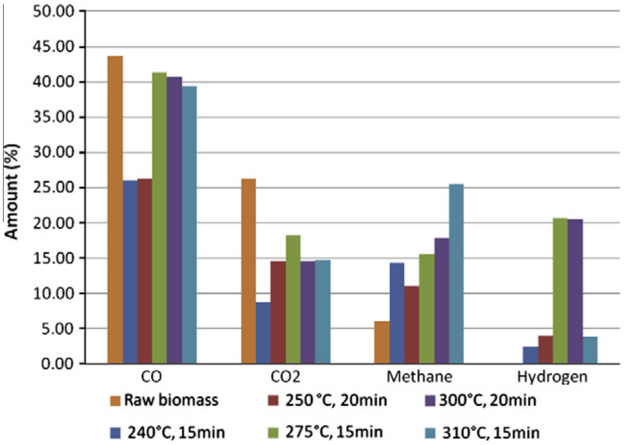

Fig. 4. The effects of torrefaction on the chemical composition of syngas from torrefied biomass pyrolysis.

carbon dioxide from pyrolysis of torrefied biomass ranged from 8.75% to 18.18% (v/v) were much lower than that from pyrolysis of raw biomass which is consistent with previous reports (Wannapeera et al., 2011). The contents of methane from pyrolysis of torrefied biomass ranged from 10.99% to 25.54% (v/v) were much higher than that from pyrolysis of raw biomass. And the large amount of hydrogen which was ranged from 2.38% to 20.61% (v/v) was detected in pyrolysis of torrefied biomass.

The torrefaction conditions also had significant effects on the syngas compositions (Fig. 4). The content of carbon monoxide from pyrolysis of torrefied biomass was obviously increased at the torrefaction temperature over 275 °C. The contents of carbon dioxide were mildly increased with the increase of torrefaction temperatures from 240 to 250 °C. At the torrefaction temperature over 275 °C, the contents of carbon dioxide were stable. The contents of methane from pyrolysis of torrefied biomass were significantly increased with the increase of torrefaction temperatures with the highest content of 25.54% (v/v) at the torrefaction temperature of 310 °C. The contents of hydrogen were first greatly increased with the increase of the torrefaction temperature then decreased at the torrefaction temperature of 310 °C. Total carbon monoxide, methane, and hydrogen were up to 68% (v/v) at the torrefaction temperature over 275 °C which indicates that the syngas from pyrolysis of torrefied biomass had high values for potential utilizations.

3.5. Mechanism analysis of torrefied biomass pyrolysis

Torrefaction can modify the structure and chemical components of biomass by removing hemicelluloses and dehydrating and partially reducing cellulose and lignin. The torrefied biomass was rich in cellulose and lignin. These changes may affect the reaction pathways of biomass pyrolysis. In the previous report the interaction between hemicelluloses and cellulose has negative effect on the formation of sugars and positive effect on the formation of furans (Wang et al., 2011). In pyrolysis of torrefied biomass this interaction might be eliminated or reduced as the hemicelluloses were removed during torrefaction. This might explain our findings in analysis of bio-oil that the pyrolysis of torrefied biomass had the selectivity for sugars production (Figs. 2 and 3). The bio-oil analysis also showed that some guaiacols were replaced by phenols in the torrefied biomass pyrolysis (Figs. 2 and 3). This implied that the torrefaction also affected the mechanism of lignin decomposition. In our previous report, the small amount of phenols in woody biomass pyrolysis was produced by the cleavage of methyl from $O{-}CH_3$ at the temperature over 471 °C (Ren et al., 2012). But in the pyrolysis of torrefied biomass this cleavage was enhanced resulting in the large amount of phenols. Hosoya et al. (2009) described the reaction pathway involving the homolysis $O{-}CH_3$ and methane production under the effects of cellulose-derived products on the lignin pyrolysis. This mechanism might be applied to this study to illustrate the significant increase of methane found in the syngas (Fig. 4).

4. Conclusions

This study investigated the effects of torrefaction on biofuel production of biomass microwave pyrolysis. The bio-oil yields were decreased with the severity of torrefaction. The compositional analysis of bio-oils showed that the torrefaction improved the sugars, phenols, and hydrocarbons production and reduced organic acids which might has potential benefits for bio-oil storage and refinery such as less hydrogen consumption. Additionally, the torrefaction enhanced the CH_4 and H_2 in syngas and reduced the CO_2 production, suggesting that the torrefaction significantly improved the syngas quality during pyrolysis of torrefied biomass.

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